Rate Constants and Temperature Dependences for the Reactions of Hydroxyl with Several Halogenated Methanes, Ethanes, and Propanes by Relative Rate Measurements

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Abstract

Relative rate data are reported for the OH abstraction reactions of 14 halogenated methanes, ethanes, and propanes. Using CH_4, CH_3CCl_3, CF_3CF_2H, and C_2H_6 as reference standards (JPL 92-20 rate constants)[1], absolute rate constants are derived and are compared with other experimental results and with transition state theory calculations of Cohen and Benson[2] and Jeong and Kaufman[3].

Introduction

Most atmospheric species which have at least one C-H bond are destroyed in the atmosphere by OH attack. To estimate the atmospheric lifetimes of such species, accurate data for the rate constants and temperature dependences are needed. Such data are especially useful when referenced to methyl chloroform, because that compound is used as a standard for atmospheric lifetimes of species removed by OH[4]. A considerable body of data has accumulated for these reactions. (See reference 1 for a compilation). The bulk of the data have been obtained by measuring the rate of disappearance of OH in the presence of the reactant. However, such measurements are frequently unable to distinguish between OH loss due to the primary reaction and other losses such as those due to impurities, secondary or side reactions, and wall reactions. As a consequence many rate constants obtained in that manner are effectively upper limits to the correct rate constants, and tend to imply shorter atmospheric lifetimes than is actually the case. Also, the uncertainty makes the data less useful for tests of theory, such as comparison of pre-exponential factors with those calculated from transition state theory[2,5] or for calibration of rate constant estimation methods such as that of Atkinson[6]. Also, collations with abstraction reactions of other species such as Cl, Br, and I may be obscured by errors in the OH database[7].

An alternative method to obtain the necessary rate constant data is to measure rate constants and their temperature dependences on a relative basis. This method has the advantage of being insensitive to impurities, secondary reactions, or wall losses which compromise the measurements based on OH loss. If CH_3CCl_3 is included in the relative database, then the results can be used for atmospheric lifetime calculations without regard to the absolute accuracy of any of the rate constants. Further, if a reliable absolute rate constant is available, such as is believed to be the case for the OH + CH_4 reaction ', then the relative data can be placed on an absolute basis by including CH_4 as a reference standard. in the present work we report relative rate measurements, traceable to both CH_4 and CH_3CCl_3, for fourteen halogenated methanes, ethanes, and propanes. In some cases the results agree very well with previous measurements based on OH loss, but often the latter are higher than those from the relative rate results.

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The experimental pre-exponential factors arc examined for their dependence on the number of hydrogen atoms in the molecules, and arc compared with recent transition state predictions.

Experimental Section

The relative rate technique used in this work has been described in several recent publications[8-10]. The method involves measurement of the fractional losses of the reactant compound and a reference compound in the presence of OI I. The OII radicals arc produced by UV photolysis of O_3 (5- 10 x 10^{16} cm^{-3}) in the presence of water vapor (3-5 x 10]^7 cm^{-3}) in a slow-flow, temperature-controlled photochemical cell. For reactants such as 1 IFC's which do not absorb 185 nm radiation, direct photolysis of H_2O at 185 nm may also be used for OII production. The 1 I-atoms produced in the H_2O photolysis arc converted to the relatively unreactive HO_2 in the presence of O_2,. The cell is 10 cm in length and 5 cm in diameter, and is either water-jacketed (for the O_3 photolysis experiments) or wrapped with heating tape and insulating material for the H_2O photolysis experiments. Residence times in the cell arc about cmc minute. To obtain high conversion ratios, experiments are sometimes operated in a stopped-flow mode where the reactant mixture is expanded into the IR cell for analysis after irradiation This method is most useful for the slower reactions, which tend to give small depletions. All experiments arc at atmospheric pressure. The rate constant ratio is obtained from the relation:

$$\frac{k_{reactant}}{k_{reference}} = \frac{\ln(DF)_{reactant}}{\ln(DF)_{reference}} \tag{1}$$

The quantity DF (depletion factor) is given by:

$$DF = \frac{(Initial\ (one. \cdot)}{(Final\ Conc.)} \tag{II}$$

initial reactant concentrations arc in the range 10^{14} to 10^{15} cm^{-3}, and depletion factors are normally about 1.1 to 1.5. Concentrations arc monitored with a Nicolet 20SX FTIR operated at 0.5 cm^{-1} resolution in the absorbance mode using a White cell with a three-meter path length. The mixture flows through a trap at about -20 C to remove the bulk of the) H_2O, which would interfere with the IR analysis. The light source is a low pressure Hg lamp. Flow controllers arc used to maintain constant flows of reactant mixture (1 O torr each of the two reactants plus 1000 torr Ar, stored in two S-liter bulbs), the O_2/O_3 input (flowing from a commercial ozonizer), and the Ar earl-icr. Argon is used because of its low quenching efficiency for $O(^1D)$. The experiments arc usually conducted in a light-on, light-off mode for repeated measurements of the depletion factors. Approximately 1 S minutes arc required for equilibration between cycles.

Reactant regeneration by secondary chemistry could be a source of error, but in the presence of O_2 (which scavenges radical products) this is improbable and there is no evidence that it occurs. Results for rat c constant ratios arc tested for any dependence on the extent of reaction, which would indicate a complication due to secondary chemistry. No such dependence has ever been found in O_2-containing mixtures. in mixtures with no O_2, Cl 1_4 regeneration has been observed, as evidenced by a decreasing Cl 14 loss with increasing extent of photolysis. However, O_2-free mixtures arc not generally used. It is also necessary for OII to be the only radical species removing the reactants. other possible reactant species arc $O(^1D)$ (in the O_3 experiments), halogen atoms, and various halo-alkoxy or peroxy radicals. The $O(^1D)$ interference is avoided by using a large excess (factor of 1000) of H_2O over the reactants.

Computer simulations show that errors less than 3% are expected under these conditions. In any case it is often possible to compare results in O_3 photolysis experiments with those from 1120 photolysis experiments. No significant difference has ever been observed in these comparisons. Errors due to halogen atoms are prevented in experiments with O_3 because of rapid scavenging by the O_3. In general, reactions of secondary radicals are unimportant because of the normally low reactivity and relatively low rate of production compared to OH. Direct photolysis of reactants is a potential complication. However, the HFCs are transparent to both 185 and 254 nm radiation, and the other HCFCs are transparent to 254 nm, which is the only wavelength used for those compounds. We often test for unsuspected complications by measuring rate constant ratios with more than one reference compound, and have not found any case in which the results differ significantly.

The experiment is very accurate for rate constant ratio determinations because the depletion factors can be measured with great precision (approximately 0.1- 0.3°/0) by the FTIR technique. The FTIR measurements of the depletion factors are based on at least two measurements, one being an absorbance measurement at a fixed wavelength of a strong IR band of the compound (sometimes two bands at-c used as a further test of consistency). Absorbance has been found to be linear with reactant concentrations for the compounds used in this wet-k. The absorbance method is accurate provided that there is no overlap with the spectrum of the second reactant, and product spectra do not interfere. Product interference is tested for by subtracting a reference spectrum of the compound in question, and noting any product spectra which may have appeared. The subtraction factor, which is the factor by which the reference IR spectrum must be multiplied for exact subtraction of the spectral features of that compound, is an additional measure of the concentration. The subtraction factor ratio is used in addition to the absorbance ratios to determine the depletion factors. The best indication of the accuracy of the measurements is the fact that results obtained with depletion factors as small as $3°/0$ do not differ significantly from those with much larger depletions.

Several factors are involved in the choice of reference compounds: (1), the accuracy of the absolute rate constant; (2), the magnitude of the rate constant (which should be similar to the rate constant to be compared); and (3), the IR spectral bands should be strong and well-defined, and should not interfere with those of the reactant. From the standpoint of absolute accuracy, CH_4 is a good choice, the rate constant having been carefully measured using high-purity samples, and with great care to avoid errors due to secondary chemistry[1]. Ethane is useful as a standard for faster reactions, the OH rate constant being about 37 times faster than that of CH_4 at 298 K, 1 however, the C_2H_6 rate constant is not known as accurately as that of CH_4, despite the fact that many studies have been reported]. Our results indicate, however, that the rate constant for C_2H_6 is consistent with that of CH_4 to within about 10%[10]. As mentioned in the introduction, CH_3CCl_3 is a standard for atmospheric lifetimes, and the rate constant has also been carefully measured[1]. We'have found that the recommended rate constants for CH_4, CH_3CCl_3, and C_2F_5I (HFC-125) are consistent to within 3% or better at 298 K, when used as common references for the same gas; for example, HFC-134a[8] or HCFC-141 b[9]. The E/R values appear to be mutually consistent to within about 75 K. These three compounds, along with C_2H_6, are the primary references for our work. The rate constants used ('Table 1) are those of the JPL 92-20 evaluation. in addition to these primary references, we also use secondary references, such as 1 HFC-134a, HFC-152a, of HFC-161, where the rate constants have been determined in our own work and are based on one or more of the primary references. These secondary references are often more suitable than any of the primary references because of the position of the IR bands or the magnitude of the rate constants.

Results

Figure 1 shows, for six representative cases, a linear dependence of the rate constant ratio (slope of the line) on the extent of reactant depletion, as expected from Equation 1. This observation tends to show that reactant regeneration and product spectral interference are not sources of error. Table 2 lists the depletions that were obtained for each reactant pair in all the present experiments. Each data point is the average of 3-4 depletion ratios, which were measured in successive light-on, light-off cycles at a given temperature. Data for the temperature dependences of the rate constant ratios are listed in Tables 3-5 for the methanes, ethanes, and propanes. These data are plotted in Figures 2-4 , and the derived Arrhenius expressions are summarized in Table 6. The resulting rate constants are listed in Tables 7-9, along with comparisons with previous measurements. Figures 5-19 show graphically the data and the comparisons with other work .

Discussion

Utility of the relative rate method. The relative rate method as used in the present work is intrinsically very simple and appears to yield quite accurate temperature dependent ratio data, even though the experiments cover a relatively small temperature range. The method is essentially immune to impurity effects and secondary reactions. in all of our studies, involving many intercomparisons and consistency checks, we have seen no evidence of any systematic errors in the method. The small standard deviations of the data as seen in Table 6 demonstrate that random errors are minor. Reproducibility of a rate constant ratio in a given experiment is normally about 30A. The reference standards we have used (rTable 1) have been intercompared in our experiments and are in excellent agreement. The derived rate data are sufficiently accurate, particularly on a relative basis, to permit some conclusions concerning rate data which were previously obscured either by experimental error or by uncertainties in the application of transition state theory. These are discussed below.

Comparisons between relative and absolute rate constants. The rate constants derived from the relative rate method are either in good agreement with absolute measurements based on OH disappearance, or otherwise are lower. "There is no case in which the relative rate constant is systematically higher than the absolute rate constant. Similar comparisons were seen in previous work.[8-10] This may be due to the influence of secondary chemistry or reactions with impurities in the absolute experiments, in which any loss of OH contributes to the measured rate constant. However, there is no clear pattern to the disagreement, and other factors may be involved. "There is no apparent correlation with the magnitude of the rate constant, which might have been expected if impurity effects or secondary chemistry are important. The 1 HFC-143a reaction rate is quite slow, but nevertheless there is generally good agreement between the absolute and relative measurements (Figure 13). On the other hand, the 1ll~C-161 rate constant is large and therefore spurious OH losses should be relatively unimportant, especially considering that no significant impurities were detected in the 11 FC-161.[12] Nevertheless, as seen in Figure 15, our results deviate considerably from the absolute measurements, particularly in the lower temperature range. It is unlikely that our rate constant for this reactant is incorrect, because it has been substantiated in previous work[10] in which we obtained relative rate data for HFC-161, relative to CH_2Cl_2, which in turn was measured relative to HFC-152a and CH_4. These data are quite compatible with our present rate constant for 1 HFC- 161.

In some cases, the relative rate constant is lower by a nearly constant factor which is independent of temperature. The data for 1 HFC-236ea (factor of about 1.7) and HFC-245ca (factor of about 1.5) are

examples of this behavior. We suspect that this is due to a constant error in the absolute measurement of the 011 loss rate, perhaps by a secondary reaction with products.

We also observe that our data always agree with the measurements of Talukdar et al.][3], but are usually somewhat lower than those of Gierczak et al.'4 and Schmoltner et al. [12] This suggests the possibility y of an operator effect.

Application to Rate Constant Estimation Methods. Because of the large number of compounds for which 011 rate constant data arc required, and the substantial cost of individual measurements, techniques such as that of Atkinson[6] have been developed for the estimation of rate constants. These methods arc based on group effects, and require calibration from existing data. However, the absolute rate constants are often substantially in error (occasionally a factor of 5 or more), and as a consequence the estimation methods arc difficult to calibrate. The relative rate data arc much more suitable for this purpose. We arc developing a modified estimation technique based on the relative rate constants (to be published separately) which shows promise of calculating 011 rate constants at 298 K with an accuracy comparable to the experimental results.

Comparison of A-factors from Experiments and Transition State Theory (TST). Table 10 compares experimental A-factors (present and earlier work)[8-10] and those from "1'S'1' calculations of Cohen and Benson[2] and Jeong and Kaufman[3]. This table includes only those compounds in which all the C-11 bonds arc identical. There arc two points of comparison to be made, one being the absolute values and the other being the relative values. The absolute magnitudes of the A-factors arc, on the average, in reasonable agreement (a factor of 2 or better). "There arc, however, some substantial individual disagreements. For example, the A-factors for CH_3CF_3, (313F, CH_3Cl, and 1 ICFCs 140 and 141 b in the Cohen and Benson predictions arc too high (about a factor of 3) for consistency with the experimental results. The exact reason for this is not obvious, other than that some of the estimated contributions to the 'I'S entropy from sources such as internal rotation must be too high, On the other hand, the very low A-factor (4.8E-13) calculated by Jeong ant{ Kaufman for HFC-134a appears to be the result of a low estimate for the entropy of the transition state (only 7.1 eu difference between the entropy of the reactant and the "1'S model , whereas replacement of 11 by OH usually produces an increase in entropy of 10 or more eu). It thus appears that attempts to estimate the entropy of the 'I'S occasionally produce large disagreements among the 'J'S"]' calculations and also with the experimental results.

A more important comparison between experiment and "1'S'1' is with regard to the relative values of the A-factors. It can be seen from Table 11 that the experimental A-factor ratios arc remarkably consistent with a simple proportionality to the number of 11-atoms. The largest deviations (still less than a factor of 2) seem to occur for molecules such as (;113CY3 and CH_3CCl_3. In these cases the relative A-factors arc low by an amount which is slightly out'side' the estimated experimental error, which is about a factor of 1.3. The ratios from '1"S predictions show no discernible dependence on the number of 11-atoms. As we have seen above, uncertainties in the "1'S entropy estimates produce substantial variations (factor of 3 or more) in the predictions. As a result, any meaningful information on the relative A-factors is obscured.

From 'Table 10 it is apparent that an A-factor per 11-atom of about 8.011-12 cm^3/molec-s can be used for molecules with a single type of C-} 1 bond. For molecules with different C-11 bonds it is necessary to know the relative contributions to the overall rate constant from the different reactive sites.

5

This information can, however, be obtained from the rate constant estimation methods and an effective A-factor can then be predicted.

{conclusions

1. The relative rate method for OH reaction t ates produces accurate and self-consistcllt rate constant data which arc well-suitcci for applications such as-tests of rate theory, calibration of empirical estimation techniques, ancl atmospheric lifetime calculations. This approach is more reliable and more economical than the absolute measurement method, which frequently and unpredictably yields incorrectly high rate constants.

2. Absolute methods based cm OH disappearance arc best suited for determination of a fcw standard rate constants (such as those for CH_4, C_2H_6, and (113CC13), which can then be used to place the relative rate constants on an absolute basis.

3. Transition state theory ususally predicts the correct order of magnitude for A-factors, but uncertaintics in the transition state entropy occasionally produce large errors.

4. For A-factor predictions, the assumption of 8.01;- 12 cm^3/molec-s pet H-atom (for cases where all C-H bonds are identical) yields a value which will usually be accurate to within a factor of 1.3.

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Table. 1. Rate Constants of the Primary Reference Compounds Used in This Work.

Reference Compound	Arrhenius Rate Constant[a]	k(298 K)
CH_4	$2.9E-12exp(-1820/T)$	$6.5E-15$
CH_3CCl_3	$1.8E-12exp(-1550/T)$	$1.0E-14$
CF_3CF_2H	$5.61E-13exp(-1700/T)$	$1.9E-15$
C_2H_6	$8.71;-12exp(-1070/T)$	$2.413-13$

(a). All from JPL 92-20.

Table 2. Ranges of depletion factors for relative rate measurements of halogen-substituted alkanes

Reactant	Reference	Depletion factor range	
		Reactant	Reference
cl HF_2Cl (HFC-22)	CH_4	1.10-1.14	1.14 -1,2.4
CHF_2Br (HFBC-22B)	CH_4	1.11-1.31	1.07-1.23
CH_3F	CH_3CF_2H (HFC-152a)	1.70-2.05	1.34- 1.s5
cl I_2F_2	CH_3CF_2H (HFC-152a)	1.20-2.01*	1.82- 8.25*
CHF_3	CHF_2CF_3 (HFC-125)	1.04 - 1.28*	1.70-4.37*
$CHClFCCl_2F$ (1 CFC-122a)	CH_3CF_2H (HFC-152a)	1.12-1.23	1.27-1,58
$CHCl_2CF_3$ (HCFC-123)	CH_3CF_2H (HFC-152a)	1.18-1.42	1.25-1.55
$CHFClCF_3$ (HCFC-124)	CH_4	1.13-1.22	1.12-1.17
$CHFClCF_3$ (HCFC-124)	$CHF2CHF2$ (HFC-134)	1.16-1.28	1.13-1.25
CH_3CF_3 (HFC-143a)	$c11$~	1.03-1.33	1.16-4.23
CH_3CF_3 (HFC-143a)	CHF_2CF_3 (HFC-125)	1.11-1.65	1,17-2.18
CH_3CF_2H (111'C-I 52a)	CH_4	1.24-2.03	1.04-1.24
CH_3CF_2H (HFC-152a)	CH_3CCl_3	1.36-2.34	1.10-1.42
CH_3CH_2F (HFC-161)	C_2H_6	1.13-1.30	1.21-1.43
CF_3CHFCF_3 (HFC-227ca)	CH_4	1.06- 1.57*	1.41- 6.89*
CF_3CHFCF_3 (HFC-227ca)	CHF_2CF_3 (HFC-125)	1.04-1.10	1.06-1,12
		1.10 - 1.70*	1.)1-1.82*
$CF_3CH_2CF_3$ (HFC-236fa)	c111'p~ (111'c-I 2s)	1.02-1.04	1.08 -1.1S
		1.06- 1.26*	1.36-2.53*
$CF_3CHFCHF_2$ (} IFC-236ca)	CH_4	1.23 - 2.00*	1.30-2.81*
$CHF_2CF_2CH_2F$ (HFC-245ca)	CH_4	1.08-1.17	1.06-1.15

* Stopped flow measurement.

Table 3. Experimental results for rate constant ratios, k/k_{ref}, for halogen-substituted methanes.

CHF$_2$Cl		CHF$_2$Br		CH$_3$F		CH$_2$F$_2$		CHF$_3$	
T(K)	k/k_{ref}[a]	T(K)	k/k_{ref}[a]	T(K)	k/k_{ref}[b]	T(K)	k/k_{ref}[b]	T(K)	k/k_{ref}[c]
298	0.777	283	1.672	298	0.543	297	0.318	298	0.132
298	0.736	298	1.549	308	0.571	309	0.320	298	0.121
307	0.755	312	1.508	321	0.573	317	0.335	317	0.145
317	0.717	322	1.399	333	0.585	323	0.330	330	0.162
332	0.700	343	1.258	345	0.609	338	0.355	347	0.173
349	0.676	368	1.159	363	0,602	357	0.368	365	0.185
363	0.611					383	0.386	383	0.208
366	0.606								

(a). Reference is CH$_4$.
(b). Reference is }IFC-152a.
(c). Reference is HFC-125.

Table 4. Experimental results for rate constant ratios, k/k_{ref}, for halogen-substituted ethanes.

CHClFCCl₂F (HCFC-122a)		CHClFCF₃ (HCFC-124)				CH₃CF₃ (HFC-143a)			
T(K)	k/k_{ref} [b]	T(K)	k/k_{ref} [a]	T(K)	k/k_{ref} [d]	T(K)	k/k_{ref} [a]	T(K)	k/k_{ref} [c]
294	0.446	298	1.164	298	1.293	298	0.212	298	0.630
294	0.467	298	1.217	298	1.180	298	0.199	313	0.653
298	0.481	313	1.134	298	1.272	314	0.210	330	0.714
308	0.460	328	1.054	298	1.244	328	0.189	351	0.755
328	0.444	345	1,013	308	1,216	346	0.241	383	0.823
345	0.425	358	0.936	321	1.194	374	0.242		
351	0.458	366	0.975	334	1.077	403	0.240		
358	0.426			356	1.092				
362	0.430			356	1.042				

CHCl₂CF₃ (HCFC-123)		CH₃CHF₂ (HFC-152a)				CH₃CH₂F (HFC-161)	
T(K)	k/k_{ref} [b]	T(K)	k/k_{ref} [a]	T(K)	k/k_{ref} [c]	T(K)	k/k_{ref} [f]
298	0.947	298	4.77	298	0.305	285	0.671
298	0.972	303	4.4S6	298	0.310	298	0.714
313	0.906	308	4.337	298	0.309	298	0.657
320	0.893	308	4.790	298	0.313	298	0.657
324	0.833	308	4.812	308	0.326	308	0.708
332	0.862	318	4.087	313	0.335	318	0.708
345	0.839	333	3.850	313	0.318	329	0.695
358	0.765	333	3.896	333	0.363	338	0.733
359	0.767	358	3.506	333	0.313	351	0.752
359	0.790	3S8	3.384	358	0.347	358	0.722
				358	0.355	364	0.762

Reference is (a) CH_4, (b) HFC-152a, (c) HFC-125, (d) HFC-134, (e) CH_3CCl_3, and (f) C_2H_6.

Table 5. Experimental results for rate constant ratios, k/k_{ref}, for halogen-su bstituted propanes.

CF3CHFCF3 (111'C-227ca)				CF3CH2CF3 (HFC-236fa)		CF3CHFCHF2 (HFC-236ca)		CHF2CF2CH2F (HFC-245ca)	
"T'(K)	k/k_{ref}[a]	T (K)	k/k_{ref}[c]	T(K)	k/k_{ref}[c]	T(K)	k/k_{ref}[a]	T (K)	k/k_{ref}[a]
296	0.243	298	0.991	298	0.198	298	0.796	286	1.154
320	0.2S5	310	0.864	298	0.192	320	0.746	286	1.1s1
338	0.242	323	0.938	306	0,186	333	0.723	298	1,241
355	0.250	347	0.934	312	0.185	350	0.706	298	1.170
361	0.224	358	0.930	323	0.208	366	0.690	310	1.157
398	0.230	3S8	0.972	333	0.210	380	0.668	310	1.142
		367	0.875	344	0.23s			319	1.117
				354	0.240			319	1.106
				355	0.246			331	1.135
				367	0.273			331	1.134
								345	1.0S6
								345	1.119
								364	1.041
								364	1.022

(a). Rcferenceis01~.
(b). Reference is HFC-152a.
(c). Reference is HFC-12S.

Table 6. Ratios Measured and Their Temperature Dependences.

Reactant	Reference	k/k_{ref} (a)	Ratio at 298 K
Halogen-substituted methanes			
CHF$_2$Cl (HFC-22)	CH$_4$	(0.24 $\pm$ 0.03)exp(342 $\pm$ 45)/T	0.76
CHF$_2$Br (HFBC-22B)	CH$_4$	(0.33 $\pm$ 0.03) exp(460 $\pm$ 3 1)/T	1.54
cl I$_3$F	HFC-152a (0.99:1	0.] 0)exp(-1743 35)/T	0.ss
c1121;2	HFC-1 52a (0.80:1	0.06)exp(-2775 24)/'1'	0.32
cl IF$_3$	HFC-125	(1.14 $\pm$ 0.08) exp(-654 $\pm$ 44)/1'	0.13
Halogen-substituted ethanes			
CHClFCCl$_2$F (1 ICFC-122a)	HFC-152a (0.31 $\pm$ "0.04)exp(117 $\pm$ 42)/'1'		0.46
c1lc1@~(1ICIJC-123)	HFC-152a (0.2S $\pm$ 0.03)exp(365 $\pm$ 36)/T		0.95
CHFClCF$_3$ (1 ICFC-124)	CH$_4$	(0.35 $\pm$ 0.04) exp(367 $\pm$ 40)/'1'	1.20
CHFClCF$_3$ (1 ICFC-124)	HFC-134 (0.46 $\pm$ 0.07) exp(300 $\pm$ 52)/'1'		1.26
CH$_3$CF$_3$ (HFC-143a)	CH$_4$	(0.43 $\pm$ 0.12)exp(-223 $\pm$ 90)/'1'	0.21
CH$_3$CF$_3$ (HFC-143a)	HFC-125	(2. 16:1 0.14)exp(-370 $\pm$ 21)/1'	0.62.
CH$_3$CF$_2$H (HFC-152a)	CH$_4$	(0.64 $\pm$ 0.13)exp(599 $\pm$ 67)/'1'	4.81
CH$_3$CF$_2$H (HFC-152a)	CH$_3$CCl$_3$ (0.65 $\pm$ o.12)exp(-220 $\pm$ 57)/'1'		0.31
CH$_3$CH$_2$F (HFC-161)	C$_2$H$_6$	(1.16 $\pm$ 0,] 3)exp(-158 $\pm$ 36)/T	0.68
Halogen-substituted propanes			
CF$_3$CHFCF$_3$ (HFC-227ea)	CH$_4$	(0.1 71 0. 05)exp(117 $\pm$ 105)/"1'	0.25
CF$_3$CHFCF$_3$ (HFC-227ea)	H FC-125 (0.83 $\pm$ 0.22)exp(38 $\pm$ 89)/T		0.94
CF$_3$CH$_2$CF$_3$ (HFC-236fa)	HFC-125 (1.26 $\pm$ 0.41)exp(-580 $\pm$ 109)/3'		0.18
CF$_3$CHFCHF$_2$ (HFC-236ea)	CH$_4$	(0.36 $\pm$ o.ol)exp(231 $\pm$ 12)/T	0.78
CHF$_2$CF$_2$CH$_2$F (HFC-245ca)	CH$_4$	(0.67 $\pm$ 0.07)exp(164 $\pm$ 34)/T	1.16

(a). Errors shown are standard deviations. Actual uncertainties arc approximately a factor of 1.3 in the A-factor ratios and 75-125 K in the E/R values.

Table *7.1* Halogenated Methanes: Derived Rate Constants and Comparisons with Previous Work.

Reactant	A-factor	E/R "	k(298 K)	Reference
CHF$_2$Cl	1.213-12.	1636	5.0E-15	Atkinson et al.[16]
(HCFC-22)	9.2E-13	1575	4.7E-15	Watson et al.'7
	9.5E-12	2315	4.0E-15	Clyne and Holt[18]
	2.111-12	1782	5.3E-15	Handwerk and Zellner[19]
			4.6E-15	Paraskevopoulos et al.[20]
	1.3E-12	1670	4.8E-15	Jeong and Kaufman[21]
	1.211-12	1650	4.7E-15	JPL,92-20
	8.1E-13	1516	5.0E-15	Orkin and Khamaganov[22]
	7.7E-13	1506	4.9E-15	This wink(a)
CHF$_2$Br	7.4E-13	1300	9.4E-15	Talukdar et al.[23]
(HBFC-22)	7.4E-13	1300	9.4E-15	JPL 92-20
	9,6]].13	1360	1.0E-14	This work(a)
c11$~			1.6E-14	Howard and Evenson[24]
(111'(:-41)			2.2E-14	Nip et al.[25]
	8.2E-12	1890	1.5E-14	Jeong and Kaufman[21]
	5.4E-12	1700	1.8E-14	JPL 92-20
	1.7E-12	1300	*2.213-14*	Schmoltner et al.'2
	2.2E-12	1449	1.7E-14	This work(c)
CH$_2$F$_2$			7.8E-15	Howard ant] Evenson[24]
(HFC-32)			1.2E-14	Nip et al.[25]
	4.4E-12	1766	1.2E-14	Jeong et al.[15]
	1.6E-12	1470	1.2E-14	Talukdar et al.[13]
	1.9E-12	1550	1.0E-14	JPL 92-20
	1.8E-12	1552	9.8E-15	'l-his work(c)
CHF$_3$			2.0E-16	Howard and Evenson[24]
(HFC-23)	3.0E-12	2910	2.0E-16	Jeong and Kaufman[21]
	6.9E-13	2300	3.1E-16	Schmoltner et al, [12]
	1.511-12	2650	2.1E-16	JPL 92-20
	6.4E-13	2354	2.4E-16	This work(d)

(a) CH$_4$, (b) C$_2$H$_6$, (c) HFC-1 52a, (d) 1 HFC-125, (c) HFC-134, (f) 1 HFC-1 61 were the reference compounds.

Table 8. Halogenated Ethanes: Derived Rate Constants and comparisons with Previous Work.

Reactant	A-factor	E/R	k(298 K)	Reference
CHClFCCl$_2$F (HCFC-122a)	7.11E-12	1158	1.5E-14	This work[c]
CHCl$_2$CF$_3$ (HCFC-123)			2.8E-14	Howard and Evenson [24]
	1.4E-12	1102	3.5E-14	Watson et al.[26]
	1.1E-12	1040	3.4E-14	Liu et al.[27]
	6.5E-13	840	3.9E-14	Gierczak et al. [14]
	1.1E-12	940	4.7E-14	Nielson[28]
	7.0E-13	900	3.4E-14	JPL 94
			3.2E-14	Zellner et al.[29]
	6.4E-13	910	3.0E-14	This work(C)
CHFClCF$_3$ (HCFC-124)			1.2E-14	Howard and Evenson[24]
	6.1E-13	1244	9.4E-15	Watson et al.[26]
	4.4E-13	1150	9.3E-15	Gierczak et al. [14]
	8.0E-13	1350	8.6E-14	JPL 94
	7.3E-13	1380	7.1E-15	This work(c)
	1.0E-12	1453	7.7E-15	This work[a]
CH$_3$CF$_3$ (HFC-143a)			1.7E-15	Marlin and Paraskevopoulos[30]
	2.1E-12	2200	1.4E-15	Talukdar et al.[13]
	1.6E-12	2100	1.4E-15	JPL 94
	1.3E-12	2043	1.4E-15	This work(a)
	1.2E-12	2070	1.2E-15	This work(c)
CH$_3$CHF$_2$ (HFC-152a)			3.5E-14	Handwerk and Zellner[19]
			3.7E-14	Nip et al.[25]
	9.6E-13	940	4.1E-14	Liu et al.[27]
	3.9E-12	1370	3.9E-14	Nielson[28]
	1.0E-12	980	3.7E-14	Gierczak et al. [14]
	1.5E-12	1100	3.7E-14	JPL 94
			3.3E-14	Zellner et al.[29]
	1.9E-12	1221	3.1E-14	This work(a)
	2.8E-12	1330	3.2E-14	This work(g)
CH$_3$CH$_2$F (HFC-161)			2.3E-13	Nip et al.[25]
	7.0E-12	1100	1.7E-13	JPL 94
	2.7E-12	750	2.2E-13	Schmoltner et al.[12]
	1.0E-11	1228	1.6E-13	This work[b]
	7.0E-12	1152	1.5E-13	This work(c)

CH$_4$, (b) C$_2$H$_6$, *(C)* HFC-152a, (d) HFC-125, (e) HFC-134, (f) HFC-161, and (g) CH$_3$CCl$_3$ were reference compounds.

Table 9.1 Halogenated Propanes: Derived Rate Constants and Comparisons with Previous Work.

Reactant	A-factor	E/R	k(298 K)	Reference
CF_3CHFCF_3	3.7E-13	1615	1.6E-15	93 Nelson et al.[31]
(HFC-227ea)	3.6E-13	1610	1.6E-15	94 Zhang et al.[32]
	3.8E-12	1596	1.8E-15	93 Zellner et al.[33]
			1.6E-15	93 Koch and Zetzsch[34]
	5.0E-13	1700	1.7E-15	JPL 94
	4.9E-13	1703	1.6E-15	This work[a]
	4.6E-13	1662	1.8E-15	This work[d]
$CF_3CH_2CF_3$	2.0E-14	906	9.6E-16	94 Garland et al.[35]
(HFC-236fa)			5.2E-16	94 Kolb et al.
	7.1E-13	2280	3.4E-16	JPL 94
	7.0E-13	2280	*3.4E-16*	This work[d]
$CF_3CHFCHF_2$	2.0E-13	1006	*6.8E-15*	94 Garland et al.[35]
(HFC-236ea)	1.0E-12	1430	8.5E-15	94 Zhang et al.[32]
	1.2E-12	1550	6.6E-15	JPL 94
	1.1E-12	1589	5.1E-15	This work[a]
$CHF_2CF_2CH_2F$	2.9E-12	1660	1.1E-14	94 Zhang et al.[32]
(HFC-245ca)	2.4E-12	1660	9.1E-15	JPL 94
	2.0E-12	1656	7.5E-15	This work[a]

(a) CH_4, (b) C_2H_6, (C) HFC-152a, (d) HFC-125, *(c)* HFC-134, (f) HFC-161 were the reference compounds.

Table 10. Comparison of some transition state theory A-factors with experimental values.[a]

Reactant	A(TST) CB[b]	A(TST) JK[c]	A(exp) This work	A(TST)/n(H) CB[b]	@Sri)/n(} 1) JK[c]	A(exp)/n(1 1) This work
CH₃Cl	1.1E-11	6.2E-12	4.4E-12[d]	3.7E-12	2.1E-12	1.5E-12
CH₂Cl₂	4.7E-12	2.8E-12	2.2E-12[d]	2.3E-12	1.4E-12	1.1E-12
	4.7E-12		3.2E-12[d]	2.3E-12		1.6E-12
CHCl₃	9.9E-13	1.2E-12	1.2E-12[d]	9.9E-13	1.2E-12	1.2E-12
CH₃F	1.1E-11	6.2E-12	2.3E-12	3.7E-12	2.1E-12	7.7E-13
CH₂F₂	4.5E-12	1.5E-12	1.8E-12	2.2E-12	7.5E-13	9.0E-13
CHF₃	1.6E-12	1.2E-12	6.4E-13	1.6E-12	1.2E-12	6.4E-13
CHF₂Cl (22)	1.4E-12	1.5E-12	7.1E-13	1.4E-12	1.5E-12	7.1E-13
CH₂FCl (31)	4.5E-12	1.5E-12		2.2E-12	7.5E-13	
CHFCl₂ (21)	1.3E-12	1.1E-12		1.3E-12	1.1E-12	
CHFClCCl2F (1 22a)			7.1E-13			7.1E-13
CHCl₂CF₃ (123)	6.3E-13		6.4E-13	6.3E-13		6.4E-13
CHFClCF₃ (1 24)	7.4E-13		1.0E-12	7.4E-13	-	1.0E-12
CHF₂CF₃ (1 25)	1.0E-12	-	5.6E-13	1.0E-12		5.6E-13
CH₂ClCF₂Cl (132b)	2.1E-12	9.3E-13		1.0E-12	4.7E-13	
CI 12 ClCF3 (133a)	2.3E-12	-		1.1E-12		
CHF₂CHF₂ (134)	2.5E-12		2.1E-12[c]	1.2E-12		1.1E-12
		-	1.5E-12[c]	1.2E-12	-	7.5E-13
			1.2E-12[c]	1.2E-12		6.0E-13
CH₂FCF₃ (134a)	3.2E-12	4.8E-13	1.5E-12	1.6E-12	2.4E-13	7.5E-13
			1.3E-12	1.6E-12		6.5E-13
			1.2E-12	1.6E-12		6.0E-13
CH₃CCl₃ (140)	7.1E-12	2.5E-12	1.8E-12[f]	2.4E-12	8.3E-13	6.0E-13
CH₃CFCl₂ (14 1b)	7.4E-12	-	1.4E-12(?)	2.5E-12		4.7E-13
			1.4E-12[g]	2.5E-12		4.7E-13
CH₃CF₃ (143a)	1.3E-11	-	1.2E-12	4.3E-12		4.0E-13
CF₃CHFCF₃ (227a)	1.2E-12	-	4.6E-13	1.2E-12		4.6E-13
			4.9E-13	1.2E-12		4.9E-13
CHF₂Br (Ha-1201)	1.4E-12	-	9.6E-13	1.4E-12		9.6E-13
			avgs:	1.9E-12	1.1E-12	7.8E-13
			St. devs:	9.9E-13	5.5E-13	3.1E-13

(a) Units are cm³/molec-sec.
(b) Cohen and Benson.[2].
(c) Jeong and Kaufman.[3] ant] Jeong et al.[15].
(d) Experimental A-factor from Hsu and DeMore.[10]
(e) Experimental A-factor from DeMore.[8]
(f) A-factor from JPL 92.-20.1
(g) Experimental A-factor from 1 luder and DeMore.[9]

Table 11. Experimental A-factor ratios compared to transition state theory predictions.

Reactant Pair	Exp.[a]	Statistical[b]	"TS (JK)	TS (CB)
$CHCl_3/CH_2Cl_2$	0.5s	0.50	0.43	0,21
$CHCl_3/CH_3Cl$	0.27	0.33	0.19	0.09
CH_3F/CH_2F_2	1.24	].5		2.4
CH_3Br/CH_3Cl	1.02	1.00		0.83
CHF_2Cl/CH_4	0.24	0.25	0,16	
CHF_2Br/CH_4	0.33	0,25		
CH_4/CF_3CFH_2	2.24	2.5	19.2	
CF_3CF_2H/CF_3CFH_2	0.48	0.50		0.31
CF_3CFH_2/CF_2HCF_2H	0.85	1.0		1.3
CF_3CF_2H/CF_2HCF_2H	0.48	0.50		0.4
$CHFClCF_3/CF_2HCF_2H$	0.46	0.50		0.3
$CHFClCF_3/CH_4$	0.35	0.25		
CHF_3/CF_3CF_2H	1.14	1.00		1.6
CH_3CCl_3/CF_3CFH_2	1.22	1.5	5.2	2.2
CH_3CCl_3/CF_2HCF_2H	0.84	1.5		2.8
CH_3CCl_2F/CH_4	0.49	0.75		
CH_3CCl_2F/CH_3CCl_3	0.79	1.00		1.0
CH_3CF_3/CH_4	0.43	0.75		
CH_3CF_3/CF_3CF_2H	2.16	3.00		13.0
CF_3CHFCF_3/CH_4	0.17	0.25		
CF_3CHFCF_3/CF_3CF_2H	0.83	1.00		1.2
$CF_3CH_2CF_3/CF_3CF_2H$	1.26	2.00		

(a). Ratios measured either directly or calculated from ratios measured against a common reference.
(b). Ratio expected for strict proportionality to number of hydrogen atoms.
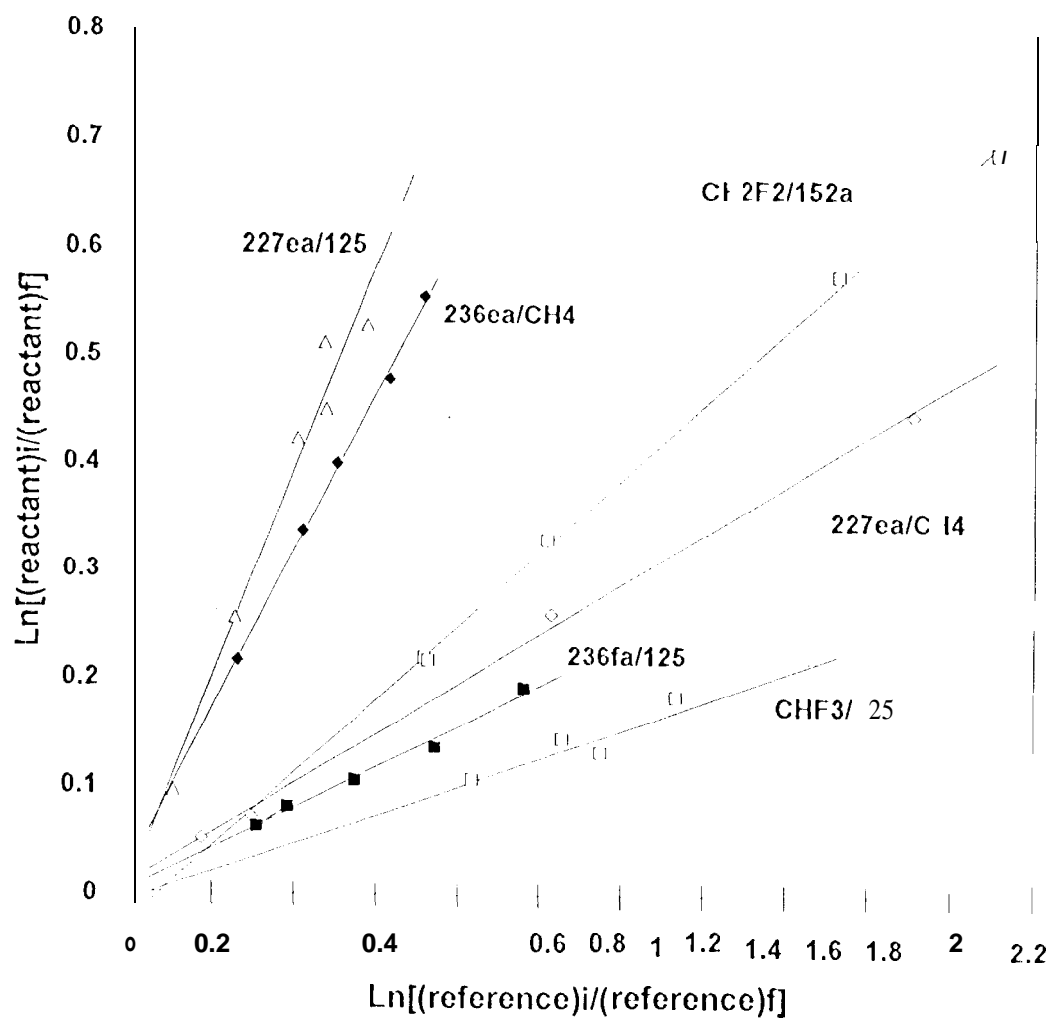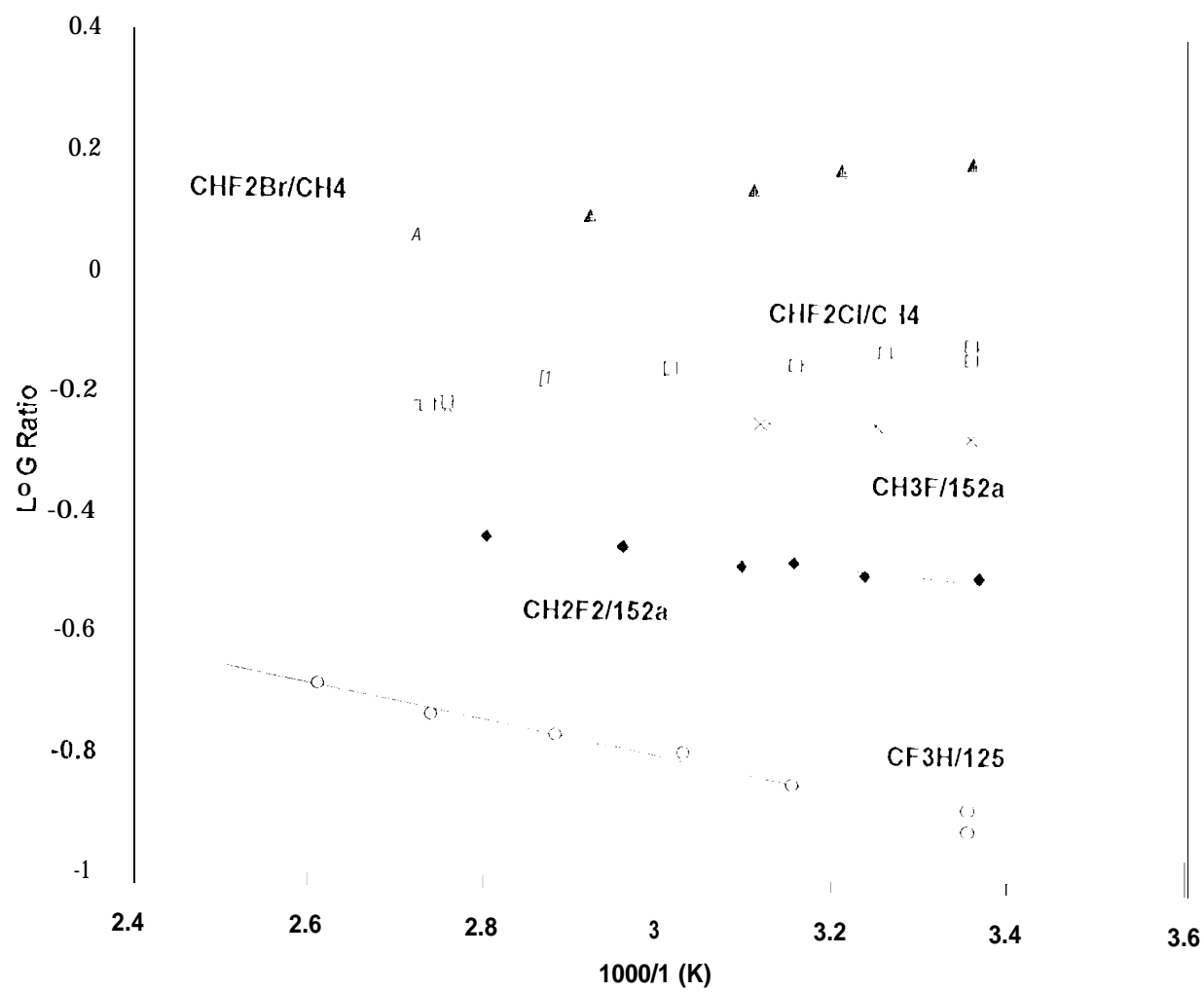
Figure 1
Hsu and DeMore
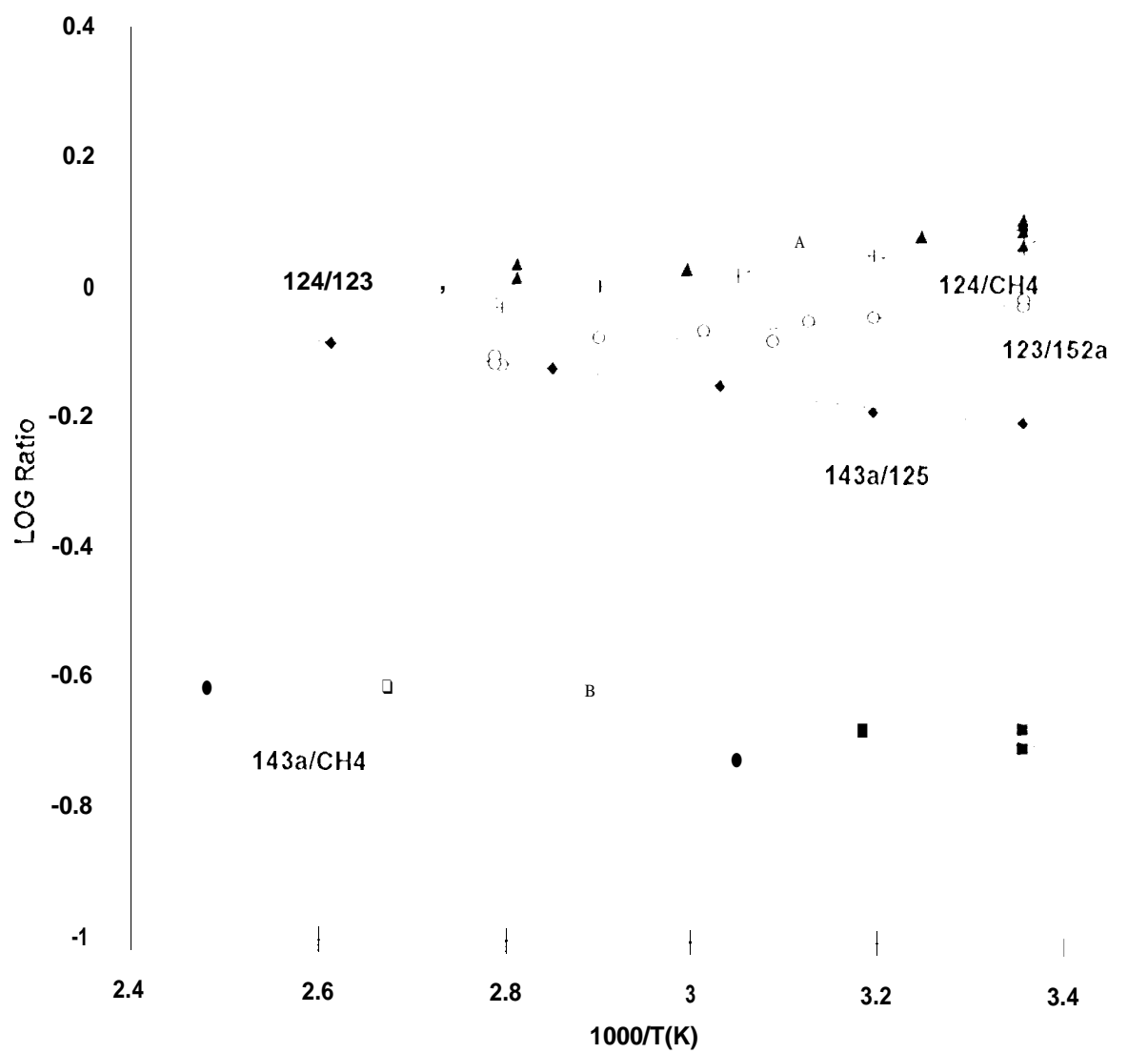
Figure 2
Hsu and DeMore

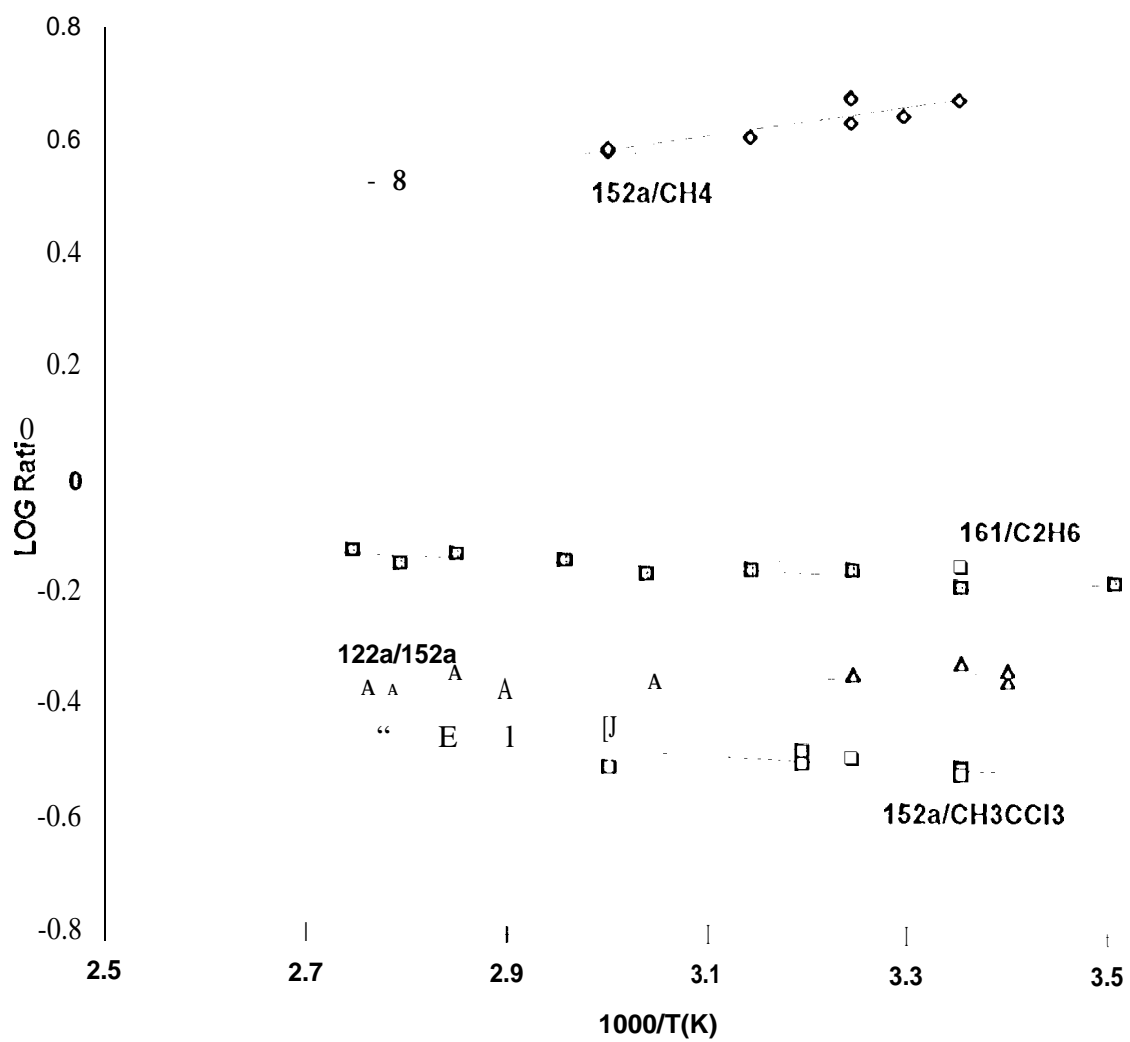Figure 3 a
Hsu and DeMore

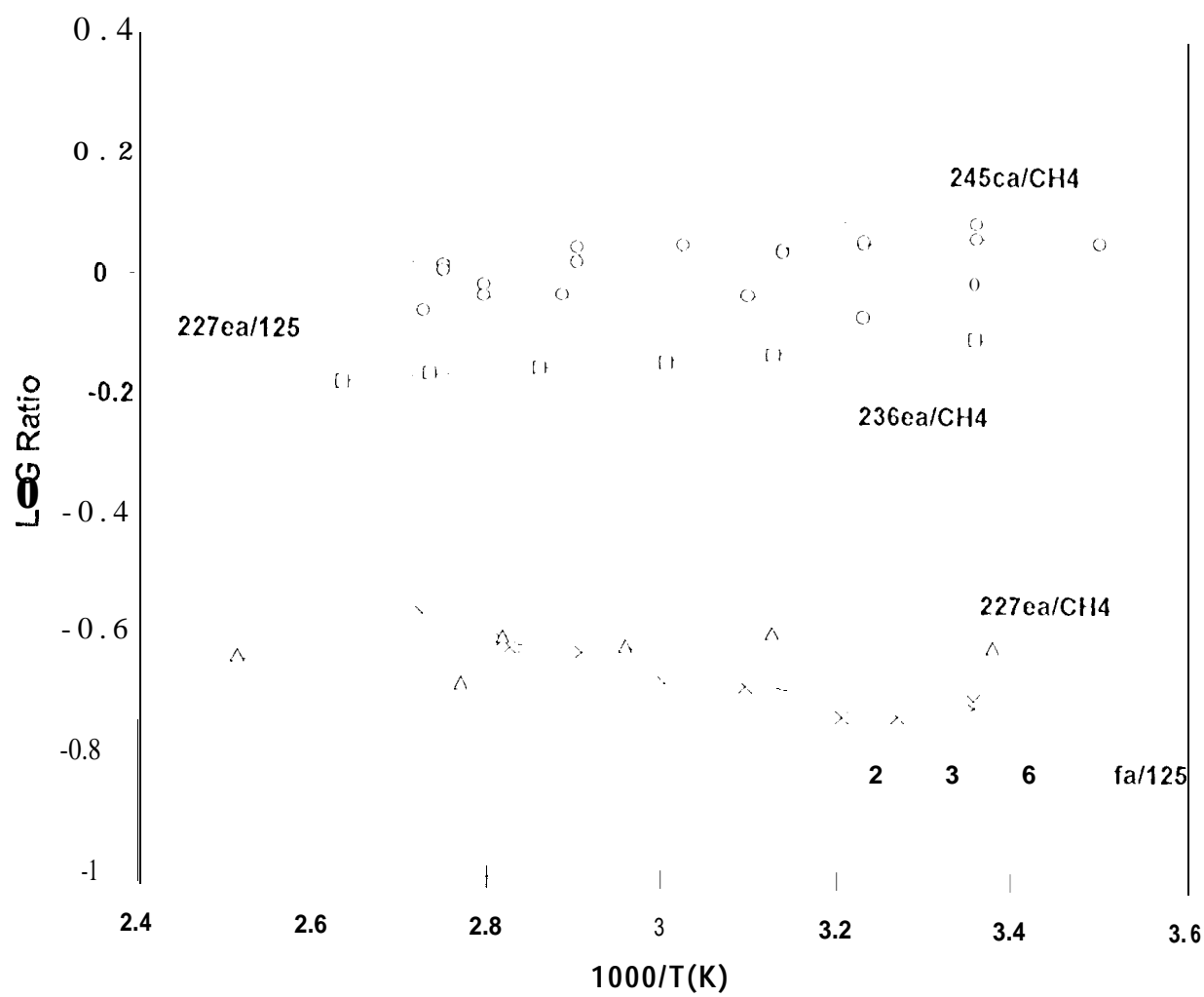# Figure 3b
Hsu and DeMore

Figure 4
Hsu and DeMore

Figure 5
Hsu and DeMore

CHF2CI (22) Data

◇ **75** Atkinson et al.

D   77 Watson et al.

x   77 Chang and Kaufman

●   78 Handwerk and Zellner

◻ 81 Paraskevopoulos et al.

A   84 Jeong et al.

+   93 Orkin and Khamaganov

    JPL, 94

o   This work/CH4
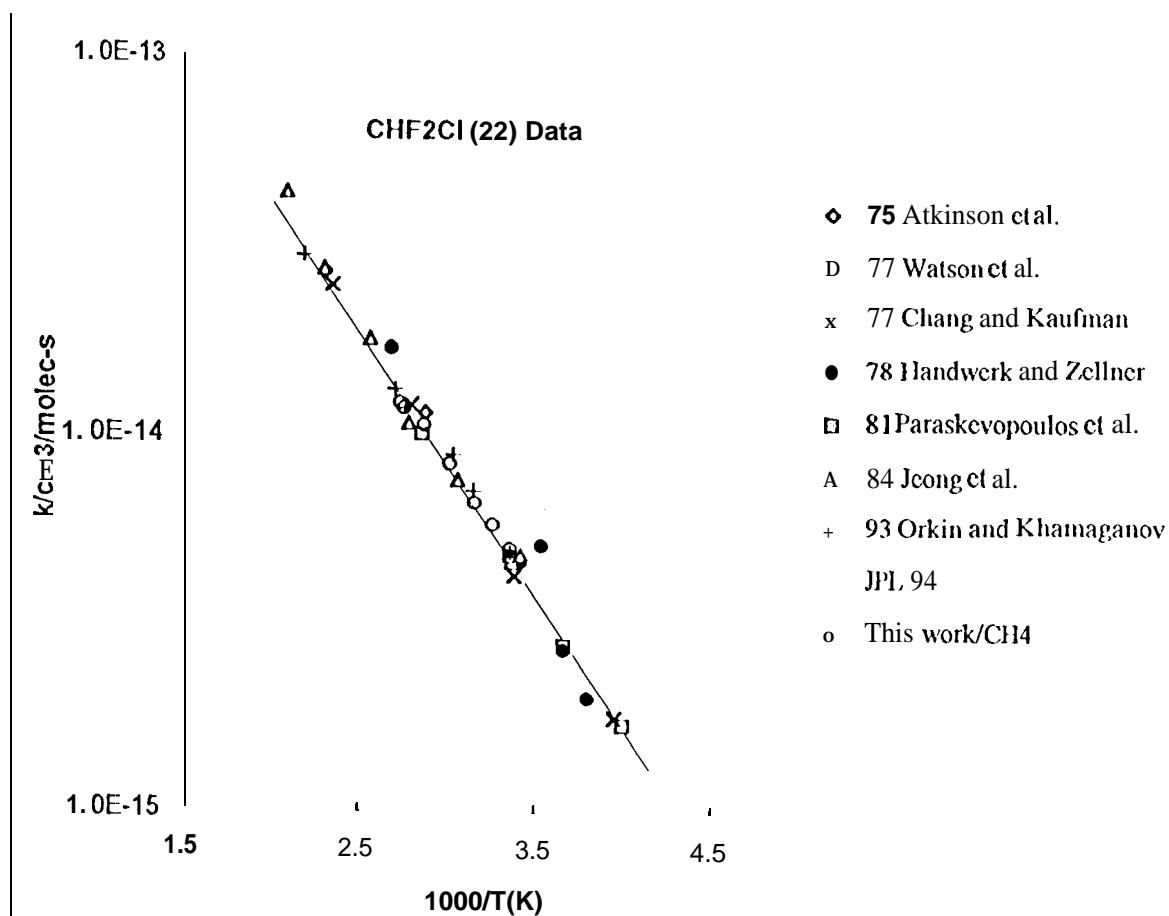
Figure 6
Hsu and DeMore

CHF2Br (22B) Data

Figure 7
Hsu and DeMore

CH3F **(41) Data**

O 93 Schmoltner et al.
x 76 Howard and Evenson
A 82 Jeong/Kaufman
D 79 Nip et al.
o This work/152a
    JPL. 94

Figure 8
Hsu and DeMore

CH2F2 (32) **Data**

◇ 93 Schmoltner et al.
❑ 91 Talukdar et al
x 761 loward a ad Evenson
+ 79 Nip el al.
   JPL 94
o **This** work/1 **52a**
A 82 Jeong and Kaufman
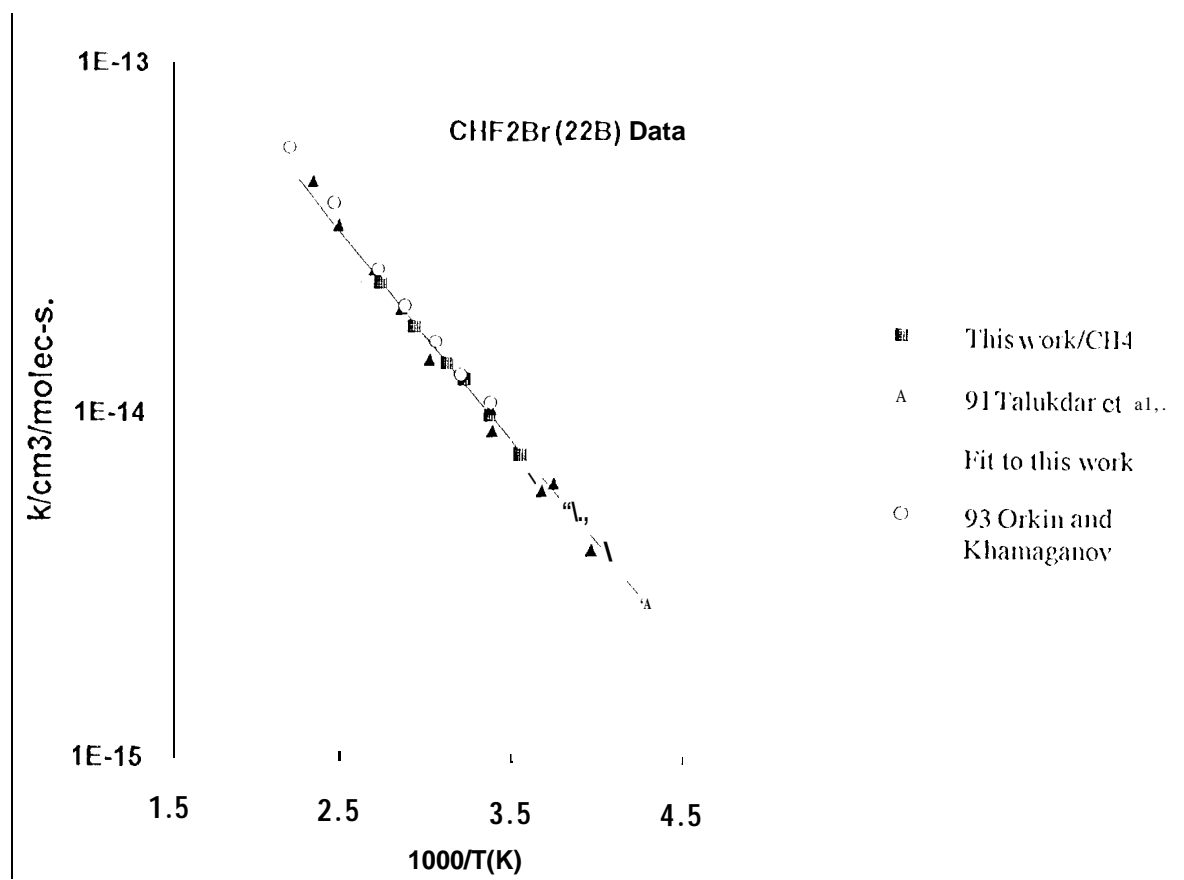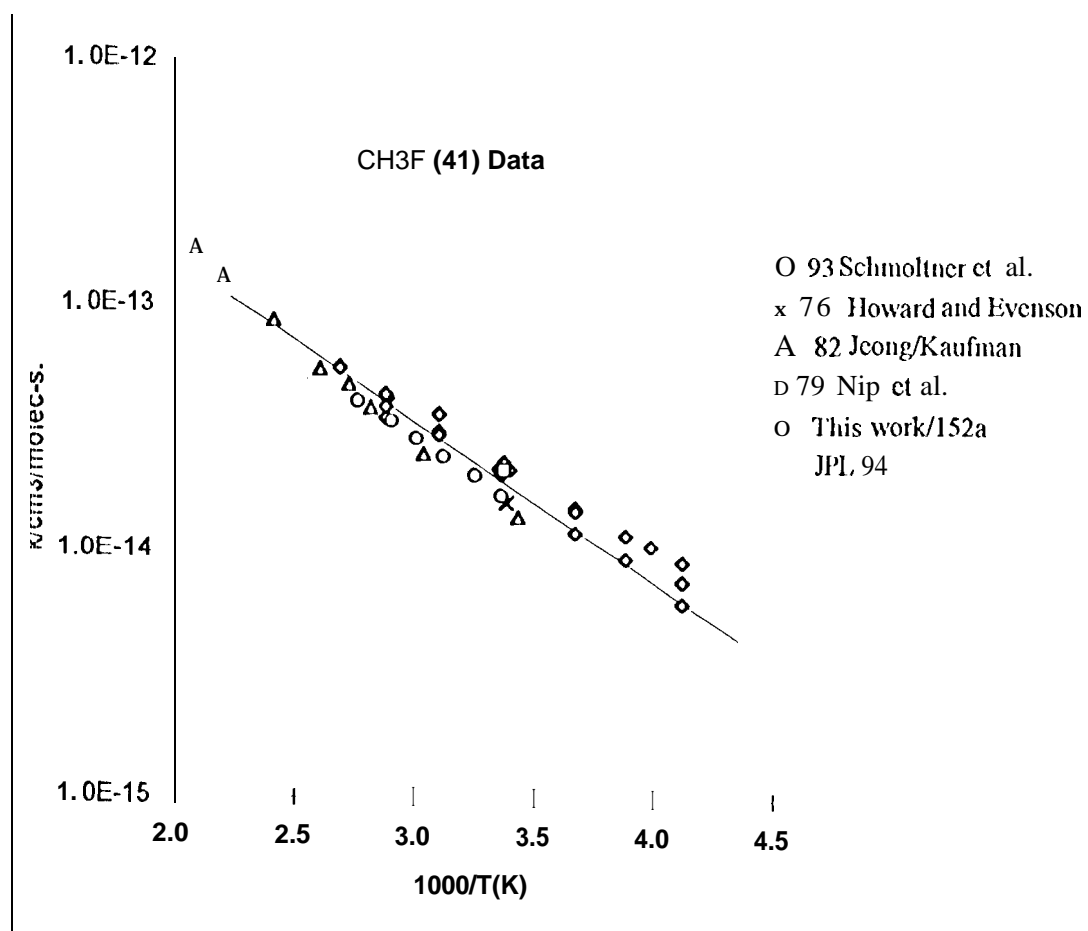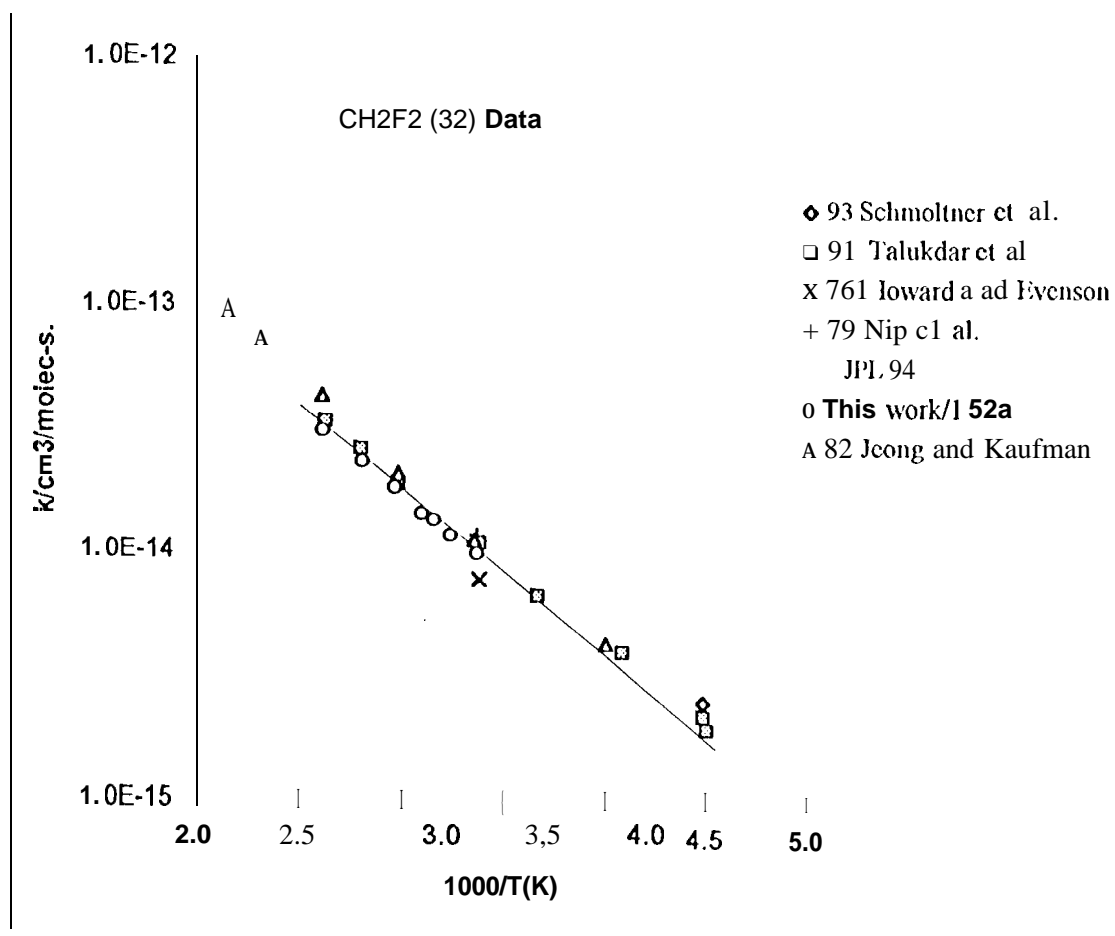
Figure 9
Hsu and DeMore

CF3H (23) **Data**

❑ 93 Schmoltner et al.
      JPL 94
A 94 Kurylo **c1** al.
x 761 Ioward and Evenson
O This work/125
o 82 Jeong and Kaufman
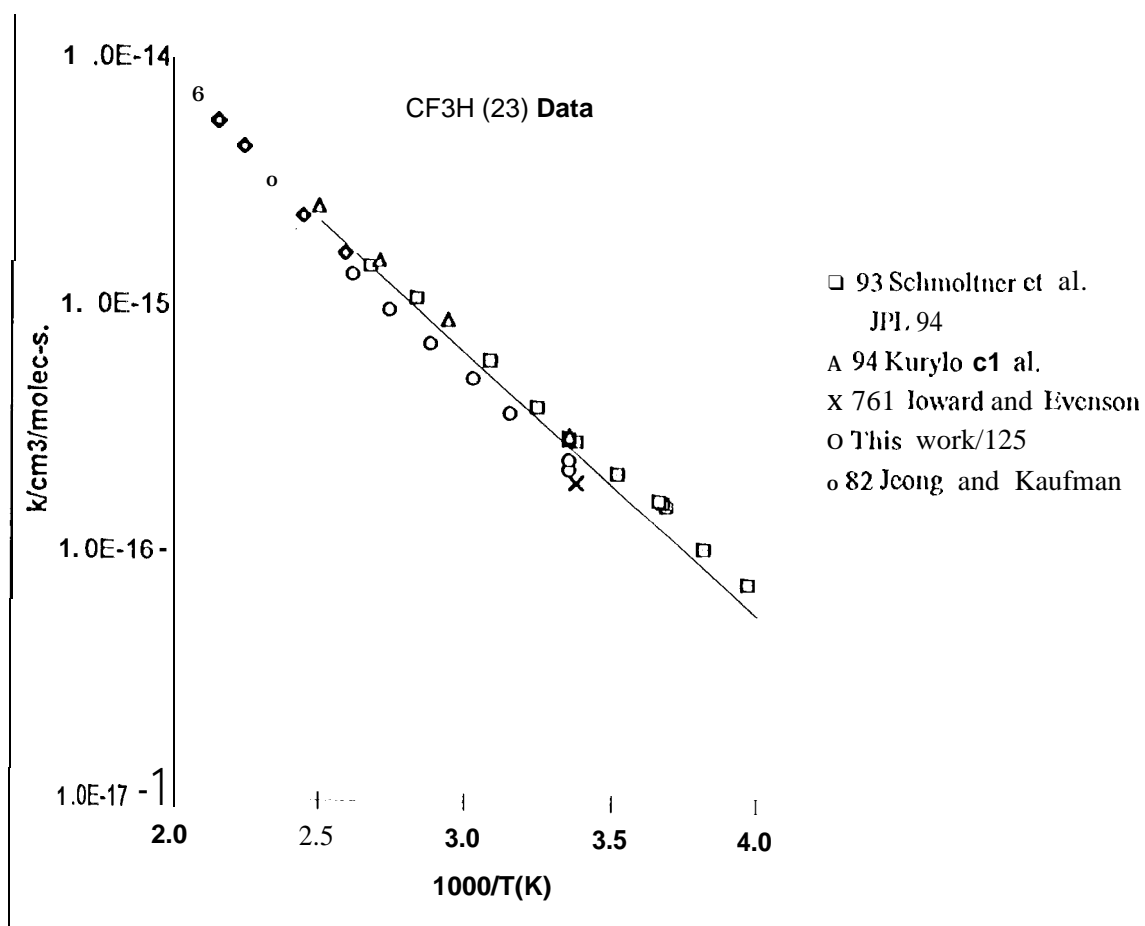
Figure 10
Hsu and DeMore
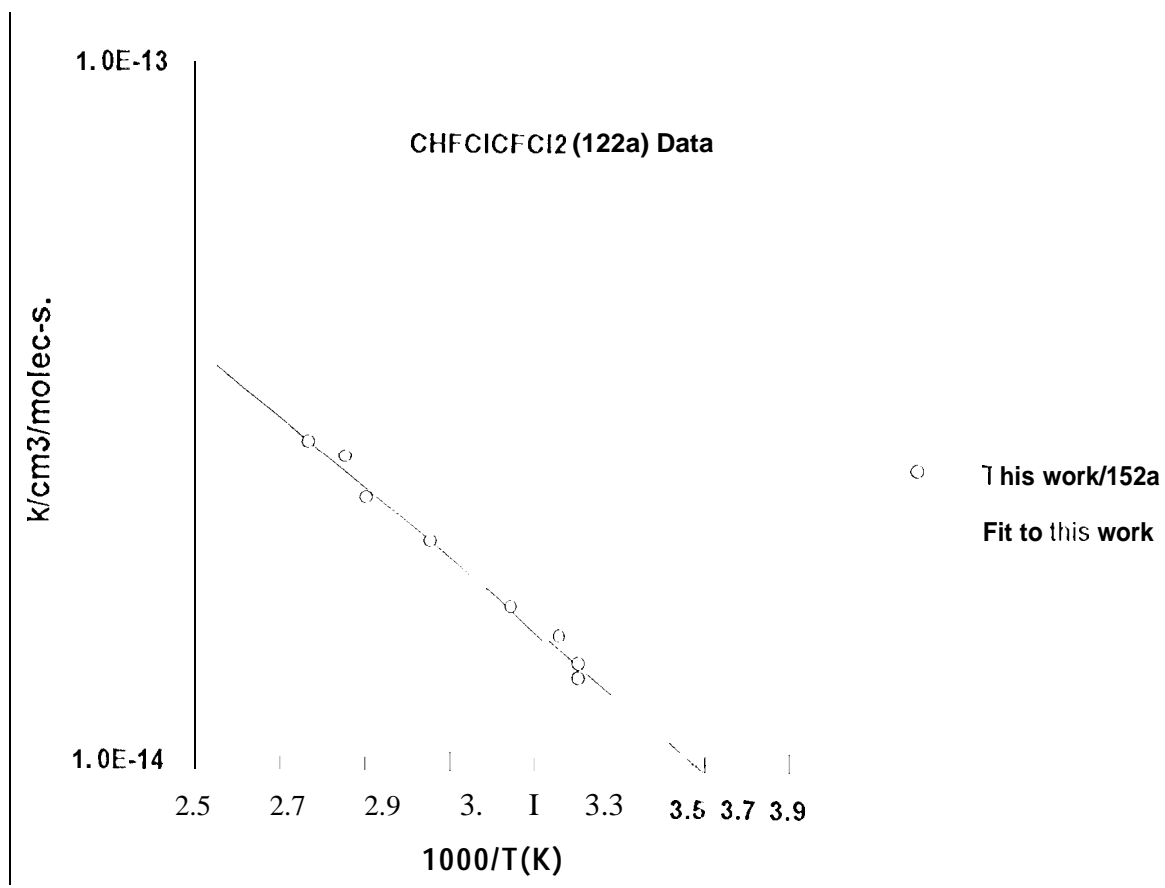
Figure 11
Hsu **and** DeMore

CHCl2CF3 (123) Data

Legend:
A 91 Gierczak et al.
o **90 Liu** et al.
U 79 Watson et al
✗ 76 Howard and Evenson
✗ 93 Zellner
   JPl.94
o **This** work/152a
+ 93 Canosa-Mas et al.

Axis labels:
- y-axis: k/cm3/molec-s. (1.00E-13 to 1.00E-14)
- x-axis: 1000/T(K) (2.00, 2.50, 3.00, 3.50, 4.00, 4.50, 5.00)

Figure 12
Hsu and DeMore

CHFClCF3 (124) Data

0 91 Gierczak et al.
o 79 Watson et al
X 76 Howard and Evenson
⎺ JPL 94
□ This work/Cl 14
A This work/134

Figure 13
Hsu and DeMore

CH3CF3 (143a) Data

D 91 Talukdar cl al,

JPL 94

A 83 Martin and
Paraskcvopolous
● This work/Cl 14

0 This work/125

Figure 14
Hsu and DeMore

CH3CHF2 (152a) Data

k/cm3/molec-s.

1.0E-12

1.0E-13

1.0E-14

2.2   2.7   3.2   3.7   4.2

1000/T(K)

0 91 Gierczak at al.

A **76** Howard **and** Evenson

❑ **90** Liu et al.

D   93 Zellner

JPL 94

o This work/CH4

O This work/CH3CCl3

x 94 Canosa-Mas et al.

Figure 15
Hsu and DeMore

CH3CH2F (161) Data

A 93 Schmoltner et al.
o 79 Nip et al
□ This work/C2H 16
  JPL 94

Figure 16
Hsu and DeMore

CF3CHFCF3 (227ea) Data

0 93 Zhang et al.
A   93 Zellner et al.
X   93 Koch and Zetzsch
       JPL 94
0 This work/1 25
❑ **This** work/Cl 14

k/cm3/moiec-s.

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Figure 17
Hsu and DeMore

CF3CH2CF3 (236fa) Data

Figure 18
Hsu and DeMore

CF3CHFCHF2 (236ea) Data

0 93 Zhang cl al.
JPL 94
0 93 Garland et al.
D This work/CH4

Figure 19
Hsu and DeMore

CH2FCF2CHF2 (245ca) Data

□ 93 Zhang et al.
JPL 94
o This work/Cl 14